

Engineering of Self-Assembled Domain Architectures with Ultra-high Piezoelectric Response in Epitaxial Ferroelectric Films**

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Substrate clamping and inter-domain pinning limit movement of non-180° domain walls in ferroelectric epitaxial films thereby reducing the resulting piezoelectric response of ferroelectric layers. Our theoretical calculations and experimental studies of the epitaxial $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ films grown on single crystal SrTiO_3 demonstrate that for film compositions near the morphotropic phase boundary it is possible to obtain mobile two-domain architectures by selecting the appropriate substrate orientation. Transmission electron microscopy, X-ray diffraction analysis, and piezoelectric force microscopy revealed that the $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ films grown on (101) SrTiO_3 substrates feature self-assembled two-domain structures, consisting of two tetragonal domain variants. For these films, the low-field piezoelectric coefficient measured in the direction normal to the film surface (d_{33}) is 200 pm V^{-1} , which agrees well with the theoretical predictions. Under external AC electric fields of about 30 kV cm^{-1} , the (101) films exhibit reversible longitudinal strains as high as 0.35 %, which correspond to the effective piezoelectric coefficients in the order of 1000 pm V^{-1} and can be explained by elastic softening of the $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ferroelectrics near the morphotropic phase boundary.

1. Introduction

Ferroelectric thin films are a subject of intensive research because of their numerous potential applications that include active components of sensors, actuators, and micro-electromechanical systems (MEMS). These applications either require a high electrical field response to an external mechanical field (direct piezoelectric effect) for sensors, or a high strain response to an applied electrical field (converse piezoelectric ef-

fect) for actuators and MEMS. However, a practical implementation of ferroelectric films in commercial devices is limited by their inferior electrical and electromechanical properties as compared to their bulk counterparts. In particular, the effects of elastic (non-180°) domain wall movement on the electromechanical response (i.e., so-called extrinsic dielectric and piezoelectric effects) are significantly less prominent in thin films.

Discussion of domain wall movement in constrained thin films has a long history. Since formation of elastic domains is a mechanism of stress relaxation in film/substrate heterostructures approaching an equilibrium,^[1] it is possible to shift the equilibrium by applying an external electrical field and thereby obtain a reversible field-induced deformation due to the changes in the domain structure.^[2] This extrinsic converse piezoelectric effect in constrained ferroelectric films has been analyzed quantitatively and its contribution to the piezoelectric modulus normal to the film/substrate interface (d_{33}) was shown to be significant and comparable to the intrinsic piezoelectric modulus of a single-domain bulk crystal.^[3] However, experimental studies revealed neither visible changes of domain structures under electrical field nor large piezoelectric effects predicted theoretically.^[4–7] Piezoelectric moduli of polydomain films are similar to those of single-domain films. Therefore, it has been concluded that the elastic domain structure in epitaxial films is less mobile compared to bulk ferroelectrics because domain walls in thin films are pinned by defects inside the film and/or by the film/substrate interface. In this paper, we present a theoretical analysis and experimental observations which demonstrate that the domain wall mobility and piezoelectric responses in epitaxial ferroelectric films can be enhanced dramatically through the engineering of special self-assembled domain architectures.

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Theoretical discussions in this paper are based on a thermodynamic analysis of constrained ferroelectric films with the three-domain architectures of elastic domains. Since ferroelectric films are commonly covered with conducting electrodes, the effects of a depolarizing field are negligible and the 90° domains act as elastic domains. The elastic domain structure in epitaxial films has been studied extensively, both experimentally and theoretically.^[8–13] Previous theoretical calculations of a converse piezoelectric effect focused on the elastic domain assemblies that consist of two domains variants (polytwins). However, a complete strain relaxation, in general, requires a formation of polydomain structures that incorporate more than two domain variants. For example, for a cubic → tetragonal transformation, a complete relaxation is attained if all the three possible domains of the tetragonal phase are involved in the formation of a polydomain structure.^[14,15]

Domain wall intersections in the three-domain structures provide additional sources of domain wall pinning that are absent in the two-domain configurations. Therefore, the two-domain architectures are expected to enhance the piezoelectric properties of ferroelectric films by increasing the mobility of domain walls, similar to the bulk ferroelectrics.^[16]

In this paper, we demonstrate that the number of domain variants in epitaxial films can be reduced from three to two by changing a crystallographic orientation of the substrate. In particular, for the $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) films with compositions near the morphotropic phase boundary (MPB), this can be achieved for the (101) substrate orientation, thereby yielding a dramatically enhanced piezoelectric response.

2. Results

2.1. Theoretical Foundation: From Three-Domain to two-Domain Structure

We consider the transformation from a cubic paraelectric to a tetragonal ferroelectric phase, which is quite generic and occurs in the PZT films used in our experimental studies. The transformation is accompanied by a self-strain that can be characterized by the tensors (Fig. 1a):

$$\begin{aligned} \hat{\varepsilon}_1^0 &= \varepsilon_0 \begin{pmatrix} \kappa & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, & \hat{\varepsilon}_2^0 &= \varepsilon_0 \begin{pmatrix} -1 & 0 & 0 \\ 0 & \kappa & 0 \\ 0 & 0 & -1 \end{pmatrix}, \\ \hat{\varepsilon}_3^0 &= \varepsilon_0 \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & \kappa \end{pmatrix} \end{aligned} \quad (1)$$

where $\varepsilon_0 = -Q_{12}P^2$ and $\kappa = -Q_{11}/Q_{12}$, Q_{11} and Q_{12} are electrostrictive coefficients, P is a polarization (P_0 is the spontaneous polarization in the absence of constraints).

For a ferroelectric film grown epitaxially on a thick cubic substrate, such that $(001)_{\text{film}} \parallel (001)_{\text{substrate}}$, the misfit is biaxial and symmetrical (Fig. 1b). The fractions of a_1 - and a_2 -domains

characterized by self strains $\hat{\varepsilon}_1^0$ and $\hat{\varepsilon}_2^0$ are equal. Hence the average self-strain is:

$$\hat{\varepsilon}(a) = a\hat{\varepsilon}_3^0 + \frac{(1-a)}{2}(\hat{\varepsilon}_1^0 + \hat{\varepsilon}_2^0) \quad (2)$$

where a is the fraction of c -domains with a self-strain $\hat{\varepsilon}_3^0$. If the film is relaxed completely by misfit dislocations in the paraelectric state, and the difference in thermal expansion coefficients of the film and the substrate is small, the film-substrate couple is stress-free just prior to the structural phase transformation. In this case, the c -domain fraction that enables a complete relaxation of the misfit stress is:

$$a_0 = \frac{\kappa - 1}{\kappa + 1} \quad (3)$$

This domain fraction is independent of domain polarization and, consequently, independent of the electrical field or temperature. Therefore, this structure remains stress-free after cooling down to room temperature.

A film relaxed in a paraelectric state can remain stress-free after transformation into a two-domain ferroelectric state if its orientation is $(h0l)$ (Fig. 1c).^[11] For example, let us consider a film oriented along the plane $x_1'x_2'$, where axis $x_2' \parallel [010]$ and x_1' forms an angle φ with $x_1 \parallel [100]$ (Fig. 1a). The film is composed of domains 2 and 3 and has an average self-strain given by Equation 4 to fit the substrate.

$$\hat{\varepsilon} = (1-a)\hat{\varepsilon}_2^0 + a\hat{\varepsilon}_3^0 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & \varepsilon_2(a) & 0 \\ 0 & 0 & \varepsilon_3(a) \end{pmatrix} \quad (4)$$

where $\varepsilon_2(a) = \kappa - a(1 + \kappa)$, $\varepsilon_3(a) = -1 + a(1 + \kappa)$, a is the fraction of c domains with self-strain $\hat{\varepsilon}_3^0$. For $a = \kappa/(1 + \kappa)$, $\varepsilon_2(a) = 0$ and the film does not change its dimension along x_2 . If the strain along the axis x_1' also equals zero, i.e.:

$$\begin{aligned} \frac{1}{2}[\varepsilon_1(a) + \varepsilon_3(a)] + \frac{1}{2}[\varepsilon_1(a) - \varepsilon_3(a)] \cos(2\varphi) &= 0, \\ \text{at } \cos(2\varphi) &= \frac{\kappa - 2}{\kappa} \end{aligned} \quad (5)$$

there is no stress in the plane of the film. Since this completely relaxed film, generally, has an irrational orientation $(h0l)$, the film/substrate interface will exhibit an array of steps which pin the domain walls and restrict their mobility.^[11] However, if $\kappa = 2$ and $\varphi = 45^\circ$, a zero-misfit plane is a close-packed (101) plane (Fig. 1c). For this interface, a plane-parallel 2-domain structure and the absence of interfacial steps enable a high mobility of domain walls, which, in turn, can enhance the extrinsic piezoelectric and dielectric responses of the film to an external electric field. For the tetragonal PZT, only structures with compositions close to the MPB have $\kappa = 2$.^[17]

Under the homogeneous approximation for the film free energy, the internal stresses due to the film/substrate misfit can be completely relaxed if different variants of the tetragonal

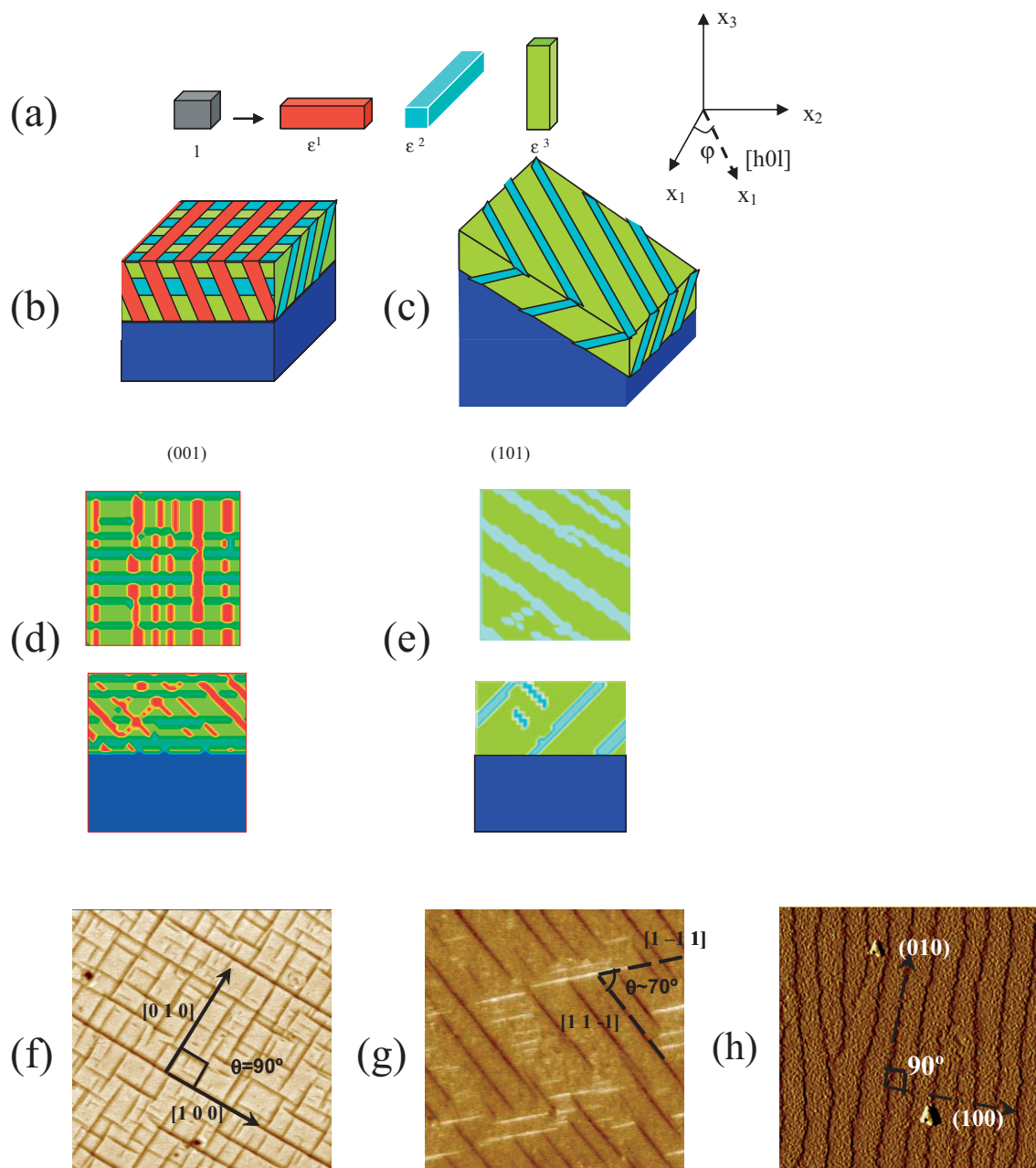


Figure 1. a) The three twin variants of the tetragonal ferroelectric phase and the $(h0l)$ -type growth plane for the 2D polydomain structure. b) and c) Schematic illustrations of domain structures in the (001)- and (101)-oriented tetragonal films, respectively. d) and e) Plane/cross-sectional views of domain structures, as calculated using phase field modeling, for the (001)- and (101)-oriented films, respectively. f) Out-of-plane piezoelectric force microscopy (PFM) image of the domain structure in the tetragonal PZT 20/80 film grown on a flat (100) SrTiO₃ substrate (the imaged area is 5 μm × 5 μm). The bright areas represent the c -domains, while the orthogonal gray stripes correspond to the a -domains that have a zero longitudinal piezoelectric response. g) and h) In-plane PFM images of domain structures in the tetragonal PZT 52/48 films grown on the flat (110) and vicinally miscut (0.8°) (100) SrTiO₃ substrates, respectively (the imaged area is 10 μm × 10 μm). Grey areas represent the c -domains, which have small shear piezoelectric responses, whereas the stripes having white/black contrast are a -domains, which have large shear piezoelectric responses. The opposite (i.e., white/black) contrast in the a -domains reflects the opposite signs of the in-plane polarizations.

phase are arranged such that the film has the same in-plane dimensions as the substrate. This approximation does not take into account domain architectures,^[9,14] which are dictated by the energy of the interdomain interfaces, the energy of the three-domain junctions, and the microstresses at the film-substrate interface.

We performed a phase-field modeling of polydomain films with different orientations to take into account the effect of interdomain interfaces and microstresses on domain architectures. The equilibrium polydomain structures were modeled by considering a phase transformation from the initial single-domain cubic phase to a product polydomain tetragonal phase.^[13]

Different crystallographic orientations of the film were introduced by rotating the self-strain tensor (1), $\varepsilon'_{ij} = a_{ik} a_{jl} \varepsilon_{kl}$, where a_{jk}, a_{jl} are the rotation matrix elements. Using the (001) orientation as a reference state, the rotation matrix for the (101) film orientation is:

$$a_{ij}^{(101)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{\sqrt{2}}{2} & \frac{\sqrt{2}}{2} \\ 0 & \frac{-\sqrt{2}}{2} & \frac{\sqrt{2}}{2} \end{pmatrix} \quad (6)$$

It is shown in previous studies that films with the (100) orientation have cellular domain architectures.^[13,14] The (100) films are divided into the cells of c -domains with polarizations along the [001] direction, which are separated by the a_1 - and a_2 -domains of equal fractions with their polarizations parallel to the [100] and [010] directions, respectively (Fig. 1d). Changing the film orientation from (001) to (101) results in a transition from the three-domain to the two-domain structure (Fig. 1e). These results prove that the domain fractions are determined primarily by minimization of the misfit stress.

Our work on the PZT 20/80 films grown on vicinal (100) SrTiO₃ substrates revealed a 2D polydomain structure with only one set of a -domains nucleating and growing at the vicinally cut steps.^[18] However, the piezoelectric measurements on these films showed no improvement in the piezoelectric response which implied that the a -domains remained “fixed” at the steps. Therefore, in order to form a mobile polydomain structure, it is necessary to have (1) a two-domain architecture to eliminate the inter-domain pinning and (2) a step-free film-substrate interface.

For the PZT system, these two conditions can be satisfied only for the MPB compositions (i.e., $\kappa = 2$) and a flat substrate with the (101) orientation (i.e., a closed-packed plane). Therefore, for experimental studies of the effects of substrate orientation on domain structure and piezoelectric/dielectric properties, we selected the PZT films with a MPB composition Zr/Ti = 52/48.

2.2. Experimental Results

Epitaxial PZT films were grown on SrTiO₃ substrates with two different crystallographic orientations, (100) and (101), using an on-axis radio-frequency (rf) magnetron sputtering technique.^[19,20] To obtain two-domain structures for both orientations, we selected the flat (110) substrates and the vicinal (100) substrates with a miscut of 0.8°. For the electric and piezoelectric measurements, Pt electrodes were fabricated via UV lithography and pulsed laser deposition.

X-ray diffraction analyses confirmed a cube-on-cube epitaxial growth of PZT on SrTiO₃ with tetragonally distorted lattices for both (001) and (101) oriented films. Figure 2 displays X-ray diffraction patterns that were used to verify the crystalline structure of the (101) films. The split 002 reflection in Figure 2b and the non-split 222 reflection in Figure 2c support a tetragonal symmetry as opposed to a rhombohedral one. The

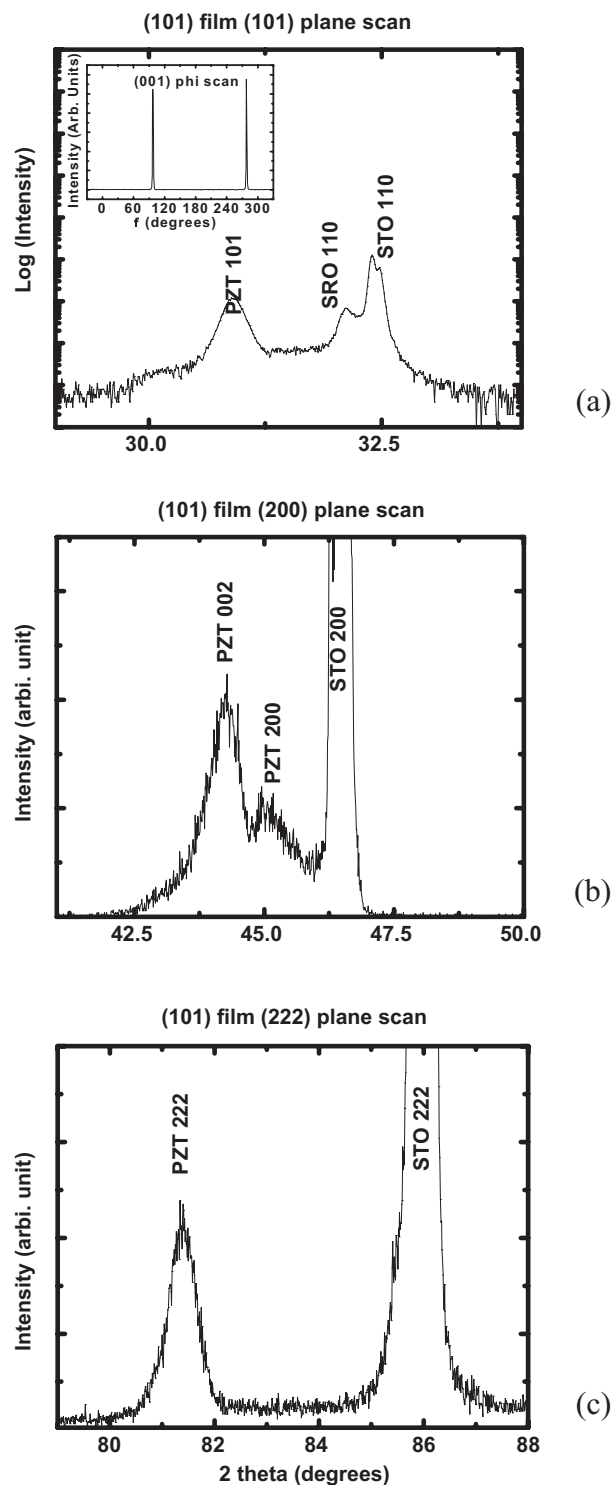


Figure 2. a)–c) X-ray diffraction patterns for the (101) PZT 52/48 film. The split 200 (b) and the non-split 222 (c) reflections support a tetragonal structure.

a -domain fractions in both (001) and (101) films were estimated to be $\approx 20\%$ from X-ray diffraction rocking curves.

Cross-sectional and plain view transmission electron microscopy (TEM) was performed for the (101) films. Figure 3a and

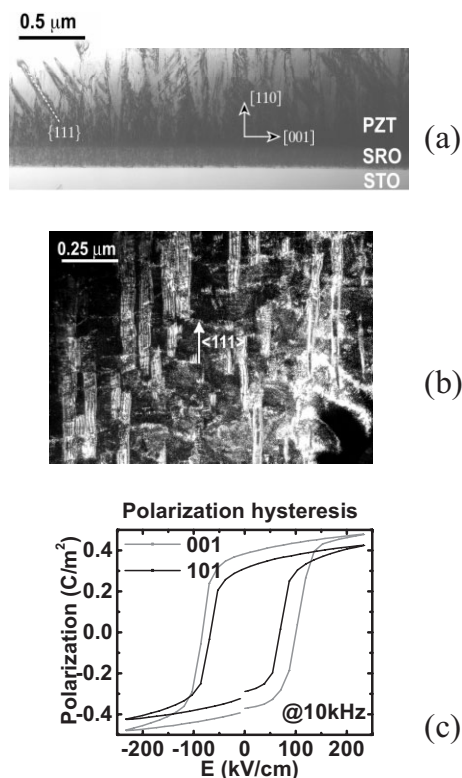


Figure 3. a) and b) Cross-sectional and plane-view TEM diffraction-contrast images of the (101) PZT 52/48 films that reveal a two-domain structure. The twin traces in both images are parallel to the $\langle 111 \rangle$ directions. Vertical pillars seen in the cross-sectional image represent subgrains that arise during growth. c) Polarization hysteresis loops for the (001) and (101) PZT 52/48 films.

b reveal two sets of strip-like parallel domains that intersect the (101) film surface along the $\langle 111 \rangle$ directions. Imaging-mode piezoelectric force microscopy further confirmed a predominant two-domain pattern with the two sets of plane-parallel domains,^[21] as presented in Figure 1g. The angle between the a -domain traces is $\approx 68^\circ$, which is close to the angle between the $\langle 111 \rangle$ traces ($\approx 70^\circ$). These observations supported the X-ray and TEM results. A piezoelectric image of the miscut (001) film is presented in Figure 1h.

Figure 3c presents the results of polarization hysteresis measurements that were accomplished using a ferroelectric tester (RT66A, Radiant Tech.) operated in the virtual ground mode. The remnant polarization (P_r) for the (101) film is smaller than that for the (001) film, as expected for a tetragonal structure. The remnant polarizations for the (001) and (101) films are 0.40 C cm^{-2} and 0.30 C cm^{-2} , respectively (leakage current densities for these films were less than 0.05 A m^{-2} for the maximum fields applied).

The piezoelectric measurements were accomplished using quantitative piezoelectric force microscopy.^[22,23] During the measurements, the AC signal was gradually increased from zero to its maximum amplitude and then decreased back to zero. The strain values were recorded at each step. The maximum AC amplitude used for each film was limited to less than

half of its coercive field in order to minimize possible contributions to a piezoelectric response from the 180° domain movement.^[6] For each film, ten continuous capacitors were measured and, for each capacitor, strain measurements were repeated 5 times. Figure 4a shows that the (001) film has a linear piezoelectric response without hysteresis. The maximum

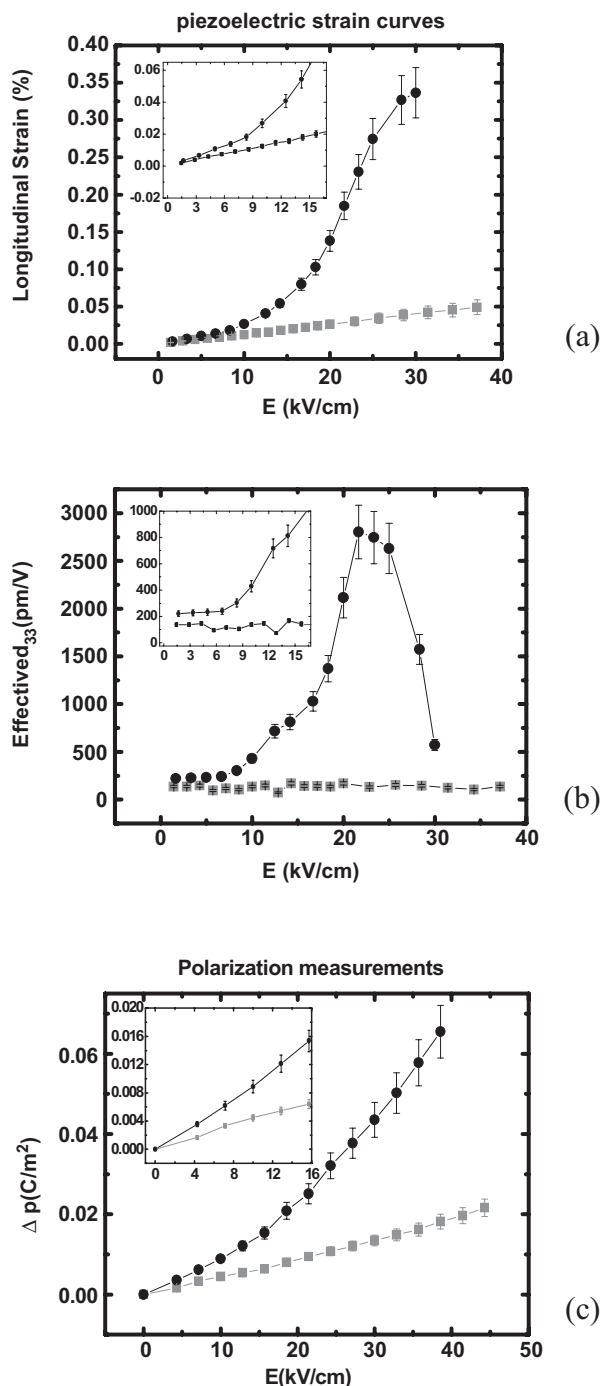


Figure 4. a) Results of longitudinal piezoelectric strain measurements under AC fields; b) Effective piezoelectric coefficient d_{33} calculated from (a). c) Results of Δp measurements. The circles and squares correspond to the results of (101) and (001) PZT 52/48 films, respectively.

strain for the (001) film is $\approx 0.04\%$ at 30 kV cm^{-1} , which corresponds to an effective d_{33} of 120 pm V^{-1} . For the (101) film, the effective low-field d_{33} is about 200 pm V^{-1} . However, as the field is increased, a strong non-linear piezoelectric response was observed. At 30 kV cm^{-1} , a strain of $\approx 0.35\%$ was obtained, which resulted in an apparent $d_{33} \approx 1200 \text{ pm V}^{-1}$. The piezoelectric strains in both films were reversible. In Figure 4b, the effective d_{33} ($=\Delta\varepsilon/\Delta E$) at each value of the electric field were calculated from the strain curve in Figure 4a. The effective d_{33} for the (001) film was almost constant, while the effective d_{33} for the (101) film varied with the applied field. It increased from about 200 pm V^{-1} at low field to $\sim 2500 \text{ pm V}^{-1}$ at 22 kV cm^{-1} , and then dropped back again to $\sim 500 \text{ pm V}^{-1}$ at 30 kV cm^{-1} .

In order to understand the origin of the observed large piezoelectric strains, sub-coercive polarization measurements were carefully performed and the ΔP values were recorded as a function of applied field (Fig. 4c). The frequency of the pulse signal and the maximum field amplitude for the polarization measurements were kept the same as those for the strain measurements. The results show that the ΔP - E curve for the (101) film is non-linear and the ΔP reaches 0.043 C m^{-2} at 30 kV cm^{-1} , whereas the ΔP - E curve for the (001) film is linear and the ΔP is only 0.015 C m^{-2} at 30 kV cm^{-1} . This is consistent with the strain-field behavior.

3. Discussion

In our recent works, the orientation dependence of intrinsic d_{33} in single-domain ferroelectric thin films was calculated for the PZT solid solutions.^[24,25] It was found that a (001) oriented film has the largest intrinsic d_{33} for both tetragonal and rhombohedral compositions, similar to the results calculated for the bulk materials.^[26,27] The intrinsic d_{33} values calculated for the PZT 50/50 tetragonal films are 120 pm V^{-1} and 167 pm V^{-1} for the (110) and (001) orientations, respectively.^[25] Considering the fractions of c domains in both films are about 80%, the contribution from the c -domain's piezoelectric response to the d_{33} are $\approx 100 \text{ pm V}^{-1}$ and $\approx 130 \text{ pm V}^{-1}$ for the (101) and (001) films, respectively. Comparison of these theoretical results with the experimental data indicates negligible contributions from the 90° domain wall movement to d_{33} of the (001) film on a vicinal substrate. At the same time, the low-field d_{33} value ($\approx 200 \text{ pm V}^{-1}$ at $E < 7 \text{ kV cm}^{-1}$) for the (101) film agrees well with the calculations based on the assumption that the 90° domain walls are mobile.^[3]

A possible explanation of the large piezoelectric response exhibited by the (101) $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ films is suggested below. In the two-domain (101) films on step-free substrates, the domain walls are mobile. Under the AC electric field, $\pm E$, there will be a contraction or expansion of the 90° domains, which will lead to a large extrinsic contribution to the longitudinal piezoelectric response. For the two-domain structure in the (001) films on vicinal substrates (Fig. 1h), the domain walls have low mobility due to the pinning by the substrate steps.

To prove the importance of a two-domain structure on the mobility of domain walls, epitaxial $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ films with

(001) and (101) orientations were prepared under the same growth conditions. The piezoelectric and dielectric measurements revealed that $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ films of both orientations have inferior electromechanical responses due to the presence of the third domain variant, and the responses of the (101) film were weaker than those of the (001) film. According to these results, both conditions (i.e., a two-domain structure and the absence of steps on a film/substrate interface) that increase the mobility of domain walls are satisfied for the (101) PZT films near the MPB composition. The same conditions can be reached for the (001) growth plane under an anisotropic stress.^[13]

While the effective d_{33} of the (101) $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ film is $\sim 200 \text{ pm V}^{-1}$ in the low electric field range (0 – 7 kV cm^{-1}), it increases for electric fields $> 7 \text{ kV cm}^{-1}$, and reaches its maximum value $\sim 2500 \text{ pm V}^{-1}$ at an electric field about 22 kV cm^{-1} . The non-linear piezoelectric response (Fig. 4a) correlates well with the non-linear dielectric response observed under the same applied electric field (Fig. 4c). This non-linearity in electromechanical properties can be explained by the field-induced softening of the film having a MPB composition. The PZT ferroelectrics exhibit a highly non-linear electromechanical behavior in the vicinity of MPB.^[28] Specifically, they become extremely soft with respect to a shear deformation.^[28] The transition from the a -domain to the c -domain is a shear process along the $\{101\}$ planes, which can dramatically enhance the elastic softening of the film. The effects of non-linear elastic properties on the electromechanical responses of polydomain thin films need further experimental and theoretical studies. The observed decrease in the d_{33} values with the increasing electric field ($> 22 \text{ kV cm}^{-1}$) can be explained by a progressive decay in the fraction of the mobile a -domains.^[29]

4. Conclusions

90° domain walls in epitaxial ferroelectric films are usually less mobile than those in the corresponding bulk materials, thereby yielding inferior electromechanical performances. The typical 90° domain structures in epitaxial ferroelectric films contain three domain variants with intersecting domain walls. In these three-domain structures, intersections of domains provide additional sources of domain wall pinning. Therefore, to enhance the mobility of 90° domain walls and to improve the piezoelectric properties of tetragonal ferroelectric films, it is necessary to reduce the number of domain variants from three to two to minimize domain wall pinning. In addition, a film/substrate interface should be a close-packed crystallographic plane to avoid the domain wall pinning by the interfacial steps. Theoretical analyses show that both requirements are satisfied for tetragonal PZT films with the compositions near the morphotropic phase boundary. Experimental studies of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ epitaxial films grown on (110)-oriented SrTiO_3 substrates demonstrate that these films exhibit two-domain architectures. The low field longitudinal piezoelectric coefficient of these films ($\approx 200 \text{ pm V}^{-1}$) is explained by assuming that domain walls are mobile. The large longitudinal strains

of $\sim 0.35\%$, that are observed under AC electric fields $\approx 30 \text{ kV cm}^{-1}$, correspond to effective piezoelectric coefficients in the order of 1000 pm V^{-1} . This behavior can be explained by the enhancement of extrinsic piezoelectric responses due to elastic softening of the MPB-PZT materials under high field. The high piezoelectric response can be excited repeatedly in a frequency range from 100 Hz to at least 100 kHz, which renders the two-domain (101) films as promising candidates for components of the next generation MEMS devices. The principles of design and engineering of domain structures in epitaxial films presented in this paper can be applied to thin films of other ferroic materials (ferromagnetics, ferroelastics or multiferroics) to achieve optimal functional properties.

5. Experimental

Prior to the PZT film deposition, a 200 nm thick epitaxial SrRuO₃ bottom electrode layer was deposited on the substrate by a 90° off-axis radio frequency (rf) sputtering technique [20]. During the film deposition, the substrate temperature was maintained at 600 °C with an oxygen pressure of 400 mTorr, followed by cooling under an oxygen pressure of 300 Torr. The thicknesses of the films were about 1000 nm. The composition of the PZT films is the same as the target as confirmed by the X-ray energy-dispersion spectroscopy (the nominal Zr/Ti ratio of the sputtering target is 52/48).

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